In-situ nanoscale characterization of cyclic reduction and reoxidation processes in CeO_x/Cu(111) model catalysts

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Cerium oxide (CeO_x) on Cu(111) is an inverse model catalytic system with a high demonstrated activity for methanol synthesis [1] from H_2 and CO_2, making it an attractive component in applications supporting the transformation to a carbon-neutral sustainable energy system based on renewables. In a reducing H_2 environment, oxygen vacancies are formed, which then activate the CO_2 [1]. Here, we have studied the interaction of H_2 and CO_2 with (111) and (100) oriented CeO_x islands on Cu(111) using intensity-voltage low-energy electron microscopy (I(V)-LEEM), micro-illumination low-energy electron diffraction (µLEED), and X-ray absorption spectroscopy combined with photoemission electron microscopy (XAS-PEEM), yielding nanoscale information about both the islands' atomic structure and local chemistry during each catalytic half-cycle. At a substrate temperature of 550 °C, exposure to H_2 leads to partial reduction whereas exposure to CO_2 facilitates reoxidation. This general chemical behavior is observed for both CeO_x orientations, yet only for the (111) facet the changes in atomic structure are fully reversible. Moreover, our experiments show that for the (111) surface subsequent redox cycles require significantly lower doses of H_2 and CO_2, indicating a conditioning effect on the reactivity of the system. Further microscopic insight is gained by determining the local oxidation state of the CeO_x(111) islands with pixel resolution (diameter ~20 nm) for the whole investigated area (300 µm²) applying a weighted superposition of I(V) reference curves [2] to the data (fig. 1, right). Contrasting our comparative studies on Ru(0001), combined I(V)-LEEM and µLEED analysis reveals a redox process involving a reversible order-disorder transition at a relative oxygen-cerium concentration of about 1.6.

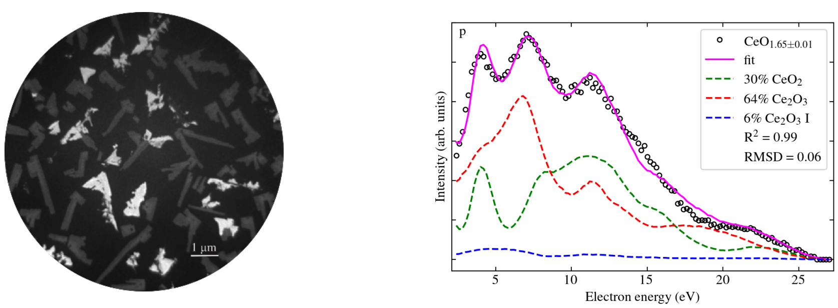

Figure 1. (left) CeO_x(111) (bright) and CeO_x(100) (gray) grown on Cu(111). (right) Decomposition of an I(V) curve (black) of a single CeO_x island into three components yielding an average oxygen-cerium concentration of $x = 1.65 \pm 0.01$.

References

[1] J. Graciani et al., Science **345**, 546-550 (2014).

[2] J. Höcker, J.O. Krisponeit, T. Schmidt, J.Falta, and J.I. Flege, Nanoscale **9**, 9352 (2017).